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Review article

Simplex optimization: A tutorial approach and recent applications in analytical chemistry

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ABSTRACT

Simplex is an optimization technique that, in a general sense, does not require the use of complex mathematical and statistical tools and can be very useful in the development of analytical methods. In this work, a tutorial reviewing the basic concepts, fundamental approach and a work guide are presented for those who contemplate simplex optimization as a tool to develop analytical methods. The characteristics and rules for applying the basic and modified simplex algorithms commonly used for optimization are also described. Some studies demonstrating the application of simplex optimization in analytical chemistry are discussed to illustrate the applicability of this technique.

Contents

1. Introduction

An optimization process aims to improve the performance of a system, a process, a procedure or a product, so that the greatest benefits can be achieved. In analytical methods, several variables (also called

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factors) can influence the magnitude of the studied response. Thus, when analytical methods are developed, they also require optimization through the investigation of variables and their respective levels [1,2].

The term optimization has traditionally been used in analytical chemistry to designate a set of experiments used to find the proper conditions for carrying out a method, in order to achieve the best possible responses, ensuring the best analytical characteristics. Moreover, it is necessary to determine whether the optimum conditions are those that result in better accuracy, higher sensitivity, lower quantification limits, the largest number of measures per time units and lower costs. Notwithstanding that, the costs of the analytical procedure should not be ignored and it is generally assumed that the best accuracy and the highest sensitivity are the most significant factors to be considered [3].

Optimization processes have been traditionally performed by monitoring the influence of one variable at a time on a given experimental response. In this type of optimization, called univariate optimization, when the level of a factor is changed, the levels of other factors of interest are kept at constant values. As a result, this technique does not allow assessing the effects of interactions between variables. In recent years, multivariate chemometric tools have been frequently applied to the optimization of analytical methods; therefore, advantages such as the reduction in the number of experiments are taken into account, hence resulting in lower costs of reagents and time consumption. There are, thus, a large number of chemometric tools, such as two-level factorial designs, mixture designs, Doehlert and Box–Behnken designs, etc., which allow multivariate optimization [4].

The simplex method suggests the optimization of various studied factors without the need to use more specific mathematical-statistical expertise as required in response surface methodology [5]. The original simplex method (basic algorithm) was developed in 1962 [6]. The first application of the simplex method in analytical chemistry occurred in 1969 [7] for the optimization of a colorimetric method in the determination of sulfur; since then, the simplex method has been satisfactorily applied to the development of analytical procedures in the determination of several analytes of interest.

This paper covers a tutorial approach about simplex optimization and its application in analytical chemistry. The initial part of the work reviews the theoretical principles and presents a work guide for those who intend to use this optimization methodology. The second part presents some examples from the literature to illustrate the use of simplex optimization in the development of analytical methods to determine various substances in different matrices.

2. Brief introduction to the simplex methodology

Simplex optimization is performed by the displacement of a geometric figure with $k + 1$ vertexes in an experimental field toward an optimal region, where k equals the number of variables in a k-dimensional domain. Simplex in one dimension is therefore represented by a line, while in two dimensions it is represented by a triangle, in three dimensions, by a tetrahedron, and hyperpolyhedrons represent multiple dimensions [8,9].

2.1. Principles of the simplex method

The principle of the simplex method is the displacement of an initial design through the experimental region studied in order to avoid regions with undesirable responses. Thus, the simplex displacement is carried out by the reflection of the experimental point showing the worst response generating a new simplex that should be once again analyzed and displaced to the optimal region. Fig. 1(a) illustrates this process in regard to the optimization of two variables: x_1 and x_2. Fig. 1(b) shows the simplex optimization regarding three variables through the displacement of the initial simplex represented by the geometric solid (tetrahedron) [10].

Sequential optimization methods such as the simplex are applied by performing few experiments at a time. The results obtained in each stage are used to support decisions in regard to experiments to be conducted later along the process that aims to reach the region of optimum response. Essentially, sequential methods comprehend simple and fast processes because they do not require mathematical functions to establish relation between factors and responses during the optimization process [11].

2.2. Characteristics of the simplex method

The simplex method is originally sequential, i.e., the next stage must only be conducted after evaluating the previous response, thereby making the method more suitable for the optimization of fast response systems. One limitation is the impossibility of working with qualitative variables. Yet, depending on the characteristics of the systems to be optimized, simplex methods are chosen because they are simple and fast. Simplex optimization is perhaps the one that best suits the most common situations encountered in the laboratory. Even though its application does not provide detailed information concerning the variables under study, it is practical and fast and allows finding the optimal region with a good safety margin [12].

Simplex optimization does not require the use of statistical tests for assessing the significance (t and F, for example) due to the following reasons: (1) if the differences in responses are large when compared with the experimental error, the simplex will move in the right direction and (2) in case the differences are small, so that they undergo influence of experimental error, the simplex will move in the wrong direction; yet, this would lead to an undesirable response and the direction would immediately be corrected by the movement rules.

2.3. Classifications of the simplex method

Some algorithms were developed for the simplex displacement along the experimental region. The original basic algorithm is the simplest and easiest to implement because it relies only on the reflection movement of the point corresponding to the worst response. The modified algorithm allows a greater range of motions and, therefore, the most accurate and efficient location for the optimum conditions. There is also the super-modified algorithm in which shape and size can be better adjusted according to the topology and the characteristics of the experimental region, thereby making the search for optimal conditions even more efficient. However, this algorithm requires the fitting of polynomial functions and that makes the mathematical treatment more complex [13,14]. The latter algorithm will not be addressed in this study.

2.4. Available software for simplex optimization

Various software packages can be used to help researchers in the application of simplex optimization. The basic simplex implicates few decision making opportunities and its movements can be easily accomplished with the help of a common electronic spreadsheet such as the Microsoft Excel®. However, the modified simplex requires the use of more specific software such as the Multisimplex® [15]. There are also free software packages for simplex optimization as the one available on the Chemkeys website [16].

3. Basic simplex

The fixed-size simplex, or basic simplex, consists of a regular geometric figure that does not vary in size during the displacement process for the optimum conditions. This characteristic of the basic simplex makes choosing the size of the initial simplex a crucial step for the efficiency of the optimization process. Thus, the experience of the